1963

# Organotin Ylids.

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# ORGANOTIN YLIDS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by
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August, 1963

## ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. Paul E. Koenig who planned and guided this investigation. He would also like to thank the many members of the graduate faculty of the Louisiana State University Chemistry Department for their consultations and assistance on special problems. Financial aid from both the National Science Foundation and the Cities Service Corporation is gratefully acknowledged. Finally, he would like to thank his parents for their constant encouragement throughout his graduate career.

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## ABSTRACT

On the basis of work done in this laboratory (1), it was reported that the most likely structure for the series of compounds known as the stannoethylenes was that of an ylid. Argument for this structure was based on the known physical and chemical properties of these compounds. The ylid structure in the stannoethylenes represent the first example of such bonding for an element in Group IV of the Periodic Table. Confirmation of the ylid nature of the methylene-tin compounds was therefore sought in the present investigation.

One of the major foundations for Calamari's proposal was the fact that the stannoethylenes seemed to form molecular addition complexes with compounds containing carbonyl functions. The reaction of the stannoethylenes with carbonyl compounds has been reinvestigated, and earlier findings (1) concerning the formation of addition complexes with aldehydes and ketones confirmed. Attempts during the present investigation to carry out the analogous reactions with esters and with carbon dioxide failed.

Oxidation of benzylidenediphenyltin gave the expected diphenyltin oxide and benzoic acid, supporting the proposed structure. Lithium borohydride failed to reduce methylene dimethyltin, but lithium aluminum hydride gave a moisture-sensitive polymeric tin hydride which was isolated as the corresponding tin hydroxide.

The stannoethylenes have been found to react quite readily with organic acids and ammonium salts of organic acids under very mild conditions to give organotin esters. There was no observable reaction with activated phenols.

Considering these observed chemical reactions in conjunction with other previously known properties, it is concluded that the ylid structure is present in the stannoethylenes.

# INTRODUCTION

It has long been recognized that classical double bonds are formed only by carbon, nitrogen, and oxygen - all members of the first short period of the Periodic Table. Elements of higher molecular weight - with the possible exception of sulfur and phosphorus (26) - form double bonds only under unusual circumstances or not at all. Chemists utilizing classical valence-bond concepts were at a loss to explain why other members of Groups IV, V, and VI did not also participate in double bond formation either with themselves or with the first members of their respective groups. With the advent of the molecular orbital theory, chemists had at their disposal a valuable tool which helped to explain the limited existence of classical double bonds. Ethylenic bonds were visualized as being formed in part through the lateral overlap of $p$ orbitals on two adjacent atoms. This type of overlap resulted in what was termed a $p\pi - p\pi$ double bond. Because of energy considerations this type of double bond is limited to those elements mentioned above. Double bonds of a non-classical nature were postulated to explain the great stability of several of the metal carbonyls (2), but these bonds were different from typical olefinic bonds. Many workers in the field believed that the molecular orbital theory offered a new

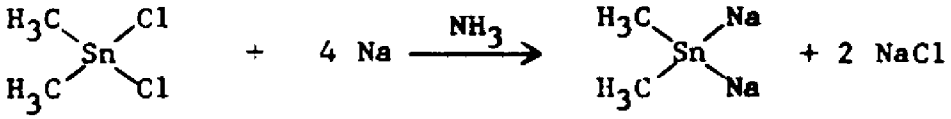
explanation for the existence and stability of compounds already well known, but did not lead to any radically different approach to the preparation of new compounds containing multiple linkages analogous to olefinic bonds. None the less, with molecular orbital concepts in mind, many workers attempted to construct molecules which would favor as much as possible the formation of double bonds of a pseudoclassical sort (2). Now, more than three decades after the elucidation of the molecular orbital theory, the number of elements known to form classical double bonds remains unchanged.

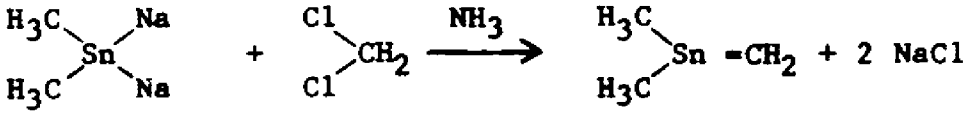
In all probability any compound which contains $\pi$ bonds utilizing d orbitals should not exhibit the characteristic properties which typify olefinic double bonds formed from $p\pi - p\pi$ interaction. Nevertheless, one particular type of organotin compound, i.e., the stannoethylenes, seemed to offer the distinct possibility of forming a double bond more nearly like those of a classical sort. Although one member of the series has long been known (20), no real attempt was made until recently to establish its structure. Some of its reported reactions could be accounted for on the basis of a classical double-bonded structure. However, the compound was quite labile, and there was reason to suppose that other members of this series of compounds might be more stable. An extension of the series to include compounds having a more favorable environment toward the stabilization of the double bond was described recently (1). All of the stannoethylenes prepared exhibited the same tendency toward rapid polymerization, and none was isolable

in the monomeric state. Because of the fact that this work demonstrated rather conclusively that the stannoethylenes were not at all similar to typical olefins, an effort was made during this investigation to establish the chemical structure of these compounds. One of the more interesting aspects of this work was the observation that these compounds seemed to form a molecular addition complex with molecules containing carbonyl functions. The formation of these addition complexes, when considered in conjunction with other assembled data, led this investigator to postulate the presence of the "ylid" structure in the stannoethylenes. Since this work was not conclusive, an effort to reexamine the data on molecular addition complexes and to study other reactions of the stannoethylenes was undertaken.

## REVIEW OF THE LITERATURE

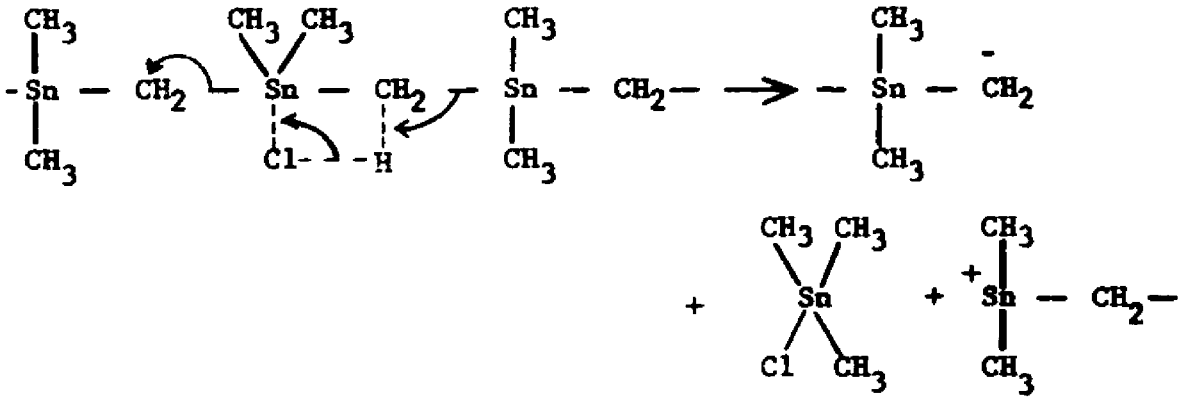
In 1925, while investigating several of the reactions of dimethyltin disodium, Kraus and Greer (20) obtained a compound, the properties of which they vaguely attributed to a tin-carbon double bond of some sort. The reaction was that of methylene chloride with dimethyltin disodium in liquid ammonia, the disodium compound having been prepared *in situ*:





The product was a thin colorless liquid which, if allowed to stand, became more and more viscous until it finally became a solid similar to resin. Several molecular weight determinations were performed, but no constant value could be obtained. The average value of a number of determinations seemed to indicate a molecular weight approximately six times that of methylene dimethyltin. Kraus and Greer assumed that the monomer was quite unstable and polymerized rather readily to give material of various molecular weights. They implied that if there was a double bond between carbon and tin initially, it was quite fragile and very susceptible to rupture followed by polymerization.

In an effort further to characterize this compound, Kraus and Greer treated the freshly formed material with hydrochloric acid. One of the reaction products was trimethyltin chloride. Kraus and Greer felt that the colorless liquid may have been methylene dimethyltin since trimethyltin chloride would result from simple Markownikov addition of hydrogen chloride to the double bond. They indicated that this evidence was not conclusive, as trimethyltin chloride could also result from the treatment of the following polymer with hydrochloric acid:



Kraus and Greer made no further effort to characterize this compound, nor did they attempt to synthesize any of its aromatic analogues. Their work was reinvestigated by Evers (6) in 1959. He confirmed Kraus' findings regarding the chemical and physical properties of methylene dimethyltin. He also extended Kraus' work to include methylene dibutyltin. Evers found that solvents other than liquid ammonia could be used, and that the resulting compounds were identical both in properties and yield to those obtained in ammonia. He offered no comment as to what the structure of the freshly formed materials might be, nor did he suggest a mechanism for the polymer formation.

Crain and Koenig (4) found that the reaction of diphenyltin disodium with 1,4 dibromobutane gave an elastomeric polymer. They also observed a reaction between diphenyltin disodium and p-dibromobenzene, but have not as yet reported conclusive results. It is believed that stannoethylene type intermediates are involved in these reactions.

While studying the preparation of methyltin tribromide from methylene bromide and tin, Kocheshkov (18) suggested that the reaction might involve dibromostannoethylene as an intermediate, i.e.,

$$CH_2Br_2 + Sn \longrightarrow CH_2{=}SnBr_2$$

$$CH_2{=}SnBr_2 + HBr \longrightarrow CH_3SnBr_3$$

He offered no proof for the existence of such an intermediate, however.

In an organotin review article (15), it is stated that "The reaction of dialkyltin disodium compounds in liquid ammonia with dichloromethane yields polymeric products." This was the extent of Gilman's comment on this reaction in what is otherwise a rather comprehensive treatise on tin chemistry.

Recently (1) the stannoethylene series has been extended to include the aromatic compounds - methylene diphenyltin and benzhydrilidene diphenyltin. Both of these compounds have properties very similar to the previously known methylene dimethyltin. They resisted all attempts at catalytic hydrogenation. They could be distilled in low yield only at low pressures (ca. .01 mm Hg), and high temperatures (ca. 180° - 220°C.). The lowest

molecular weights obtained for these compounds indicated that they were pentamers. In an attempt to establish the structure of these compounds, it was found that they seem to form molecular addition complexes with compounds containing carbonyl functions.

Other than the preceding references, no other mention of the stannoethylenes was found in the literature.

## DISCUSSION

Until recently (1), none of the investigators in the field of organotin chemistry has seen fit to comment on the structure of the freshly formed stannoethylenes (6), (15), (20). In the only structural investigation reported thus far (1), the original work of Kraus and Greer (20) was repeated and their findings verified. In this work an attempt was made to correlate the physical and chemical properties of the stannoethylenes and to determine if any conclusion could be drawn regarding their structure. Calamari (1) considered five plausible structural possibilities for these compounds: a cyclic structure, a diradical, a classical olefinic structure, a pseudoclassical double bonded structure, and an ylid structure. The cyclic structure was eliminated by virtue of the fact that the stannoethylenes are unstable and have variable physical properties. The free radical possibility was not considered valid since the reactions may be run in the presence of free radical inhibitors. From theoretical considerations and the apparent lack of classical olefinic properties, the $p\pi - p\pi$ double bonded structure was ruled highly improbable. Since no other examples of covalent $p\pi - d\pi$ bonding are known to exist, the properties of a compound containing such a bond were difficult to predict. Nonetheless, this investigator felt it was reasonable that such a hypothetical $p\pi - d\pi$ bond would be stabilized by

conjugation. In none of the aromatic analogues of methylene dimethyltin was resonance stabilization detected; therefore, the existence of a pure $p\pi - d\pi$ structure was deemed unlikely. Calamari (1) concluded that of the five plausible structures for the stannoethylenes, that an ylid was the most likely. This conclusion was strengthened by the fact that several of the stannoethylenes were apparently able to form molecular complexes with compounds containing carbonyl functions.

It was felt that while this investigation (1) seemed to indicate the existence of an ylid structure, it was not conclusive, and further work might be done to establish more firmly this structure. Before the ylid structure in the stannoethylenes is considered, the nature of known ylids will be discussed.

Staudinger and Meyer (30), while studying the chemistry of organo-phosphorus compounds, found that triphenylphosphine reacts with diphenyldiazomethane:

$$Ph_3P + Ph_2CN_2 \longrightarrow (Ph_3P = CPh_2) + N_2$$

These investigators felt that this reaction should result in the formation of a pentacovalent phosphorus compound as shown; however, they were not able to isolate any benzhydrilidenetriphenyphosphorus. The only products found were triphenyphosphine and tetraphenylethylene. The presence of these compounds was explained by assuming a disproportionation of the intermediate benzhydrilidenetriphenylphosphorus:

$$2(Ph_3P = CPh_2) \longrightarrow 2Ph_3P + Ph_2C = CPh_2$$

These investigators also tried to prepare pentaethylphosphorus by reacting diethylzinc with tetraethylphosphonium iodide. The only identifiable products were triethylphosphine, butane, and zinc iodide:

$$(C_2H_5)_2Zn + (C_2H_5)_4P^+ I^- \longrightarrow (C_2H_5)_3P + C_4H_{10} + ZnI_2$$

The presence of these compounds was again explained on the basis of a disproportionation of the intermediate ethylidenetriethylphosphorus.

This work was reinvestigated and confirmed by Coffman and Marvel (3). They discovered an alternate method of preparation for these reactive pentacovalent phosphorus intermediates. It consisted in the removal of a proton from the $\alpha$-carbon of an "onium" salt by the attack of a carbanion. The reagents employed by these investigators were triphenylmethyl sodium and butyl lithium. A typical example of their synthetic method is given by the reaction of tetraethylphosphonium iodide with triphenylmethyl sodium:

$$(C_2H_5)_4\overset{+}{P}\ \overset{-}{I} + Na^+\ \overset{-}{C}Ph_3 \longrightarrow (C_2H_5)_3P = \underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}} + Ph_3CH + NaI$$

Coffman and Marvel (3) also found that ammonium as well as phosphonium compounds would undergo proton abstraction by carbanions. Tetramethylammonium iodide when treated with butyl lithium formed a white ether-insoluble precipitate. This material was extremely reactive and was readily oxidized by air to trimethylamine oxide:

$$(CH_3)_4\overset{+}{N}\ \overset{-}{I} + C_4H_9\overset{-}{Li}\overset{+}{} \longrightarrow (CH_3)_3N = CH_2 + C_4H_{10} + LiI$$

This versatile synthetic method was later developed by Wittig (35) into a very convenient method of preparation of these compounds. He found that if phenyllithium was used as the source of the abstracting cation, the reaction proceeded quite smoothly at low temperatures:

$$R_3\overset{+}{P}CH_3\ \overset{-}{Br} + PhLi \longrightarrow R_3P = CH_2 + PhH + LiBr$$

It is the Wittig modification of the Coffman-Marvel method which is used today for the preparation of these compounds.

Ingold (16) proposed that the intermediate which previous workers (3), (30) had prepared was not really a structure in which phosphorus or nitrogen was doubly bonded to carbon in the usual sense, but rather a resonance hybrid of a doubly bonded structure and a polarized structure such as that proposed for the trialkylamine oxides:

$$R_3N = O \longleftrightarrow R_3\overset{+}{N}\text{-}\overset{-}{O}$$

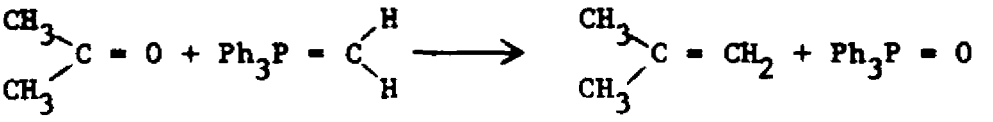
He reasoned that if the intermediate was very soluble in solvents of low dipole moment, then the doubly bonded resonance form made a greater contribution to the true structure than the polarized resonance form. If the intermediate was relatively insoluble in solvents of low dipole moment, then the converse was true. The organophosphorus intermediates, i.e., benzhydrilidenetriphenylphosphorus (3) and also ethylidenetriethylphosphorus, were much

more soluble in ethyl ether than was methylenetrimethylnitrogen. This seemed reasonable since phosphorus was known to be able to expand its octet of electrons, while nitrogen could not, thereby increasing the contribution which the doubly bonded resonance form makes in the case of phosphorus.

Ingold proposed the name "ylidide" for compounds containing semi-polar bonds to carbon. The term "ylid" was suggested by Wittig (33). Consider the general formula $R_x\overset{+}{M} - \overset{-}{C}R'_2$. The covalent part of the structure is termed "yl" as in "alkyl." The polarized portion is referred to as "ide" in the usual convention for binary ionic salts. Hence, the name "ylide" or "ylid" is determined. The term has appeared in both spellings in the literature. Wittig's suggested spelling was "ylid." In recent papers (17), (31), authors have also used the "id" ending, although the "ide" is perhaps more descriptive to American chemists. So far, the existence of ylids has been demonstrated only for elements in Groups V and VI of the Periodic Table.

Reactions of ylids with carbonyl compounds.- Of the many varied reactions of ylids which have been reported in the literature (23), (24), (17), (31), (32), (33), (34), (35), (36), (37), perhaps the best known was discovered by Wittig (35). It consists of addition of the ylid to a carbonyl group with the formation of an addition complex which upon heating gives the corresponding oxide and an olefin. Consider, for example, the reaction of acetone and triphenylphosphine methylene to give isobutylene. The

overall reaction is as follows:



Calamari (1) in an attempt to demonstrate that the ylid structure was present in the stannoethylenes, reacted methylenedimethyltin with cyclohexanone. Had the reaction proceeded in the same way as the Wittig reaction, then cyclohexene should have been obtained as one of the reaction products. Instead of an olefin, a rather stable molecular addition complex was formed, the structure of which was proposed but not proved (1).

Calamari (1) also reacted methylenediphenyltin with formaldehyde. The reaction proceeded in much the same manner as that of methylenedimethyltin with cyclohexanone in that a molecular addition complex was formed.

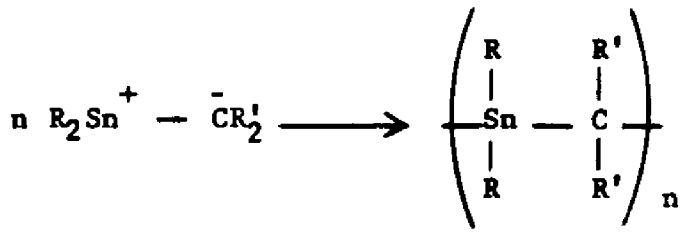
In the present investigation these two reactions have been repeated and the nature of the molecular addition complexes established more firmly, as follows:

Methylenedimethyltin was prepared in the usual manner, but it was not isolated from the ammonia-tetrahydrofuran mixture. An excess of cyclohexanone was added and the addition complex formed. It is significant to mention that upon filtration of the reaction mixture very little polymeric material remained, in contrast to the behavior observed in the absence of carbonyl compounds. Thus, when methylenedimethyltin is prepared in the absence of molecules containing carbonyl functions, filtration of the reaction mixture

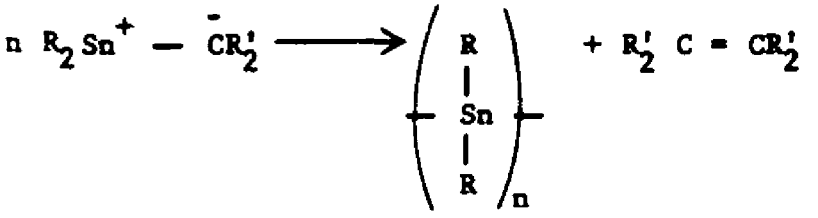
results in the deposit of much tetrahydrofuran-insoluble residue in the filter cake. This polymeric residue presumably consists of dimethyltin and its oxides and hydroxides. About one-half of the tin under the normal conditions for the preparation of the ylid appears in this unreactive side product.

On the other hand, in the presence of cyclohexanone, virtually no tetrahydrofuran-insoluble residue was found. This observation may be explained by consideration of the following facts.

The ylid is formed in a mixture of ammonia and tetrahydrofuran, the temperature of which is quite low, ca. -33°. Since the ylid structure consists of a semi-polar bond involving a separation of charge, then ion solvating media, such as ammonia, should tend to stabilize this species. When the ylid is isolated, the ammonia is first evaporated. After all the ammonia has been removed, the resulting tetrahydrofuran solution is filtered at room temperature. Thus, in the process of isolation of the ylid, two factors favoring the stabilization of the ylid have been removed, i.e., the low temperature and the presence of an excellent ion-stabilizing solvent. The monomeric ylid may decompose along two possible routes. It may simply polymerize:

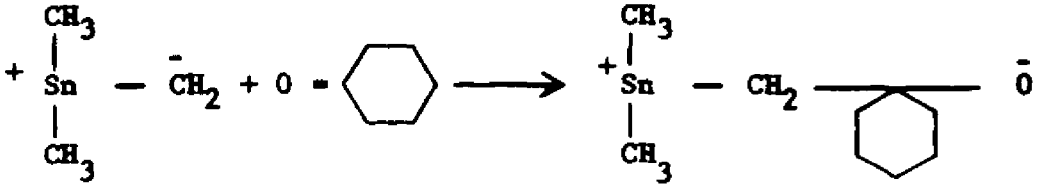


It is also possible for the ylid to disproportionate:

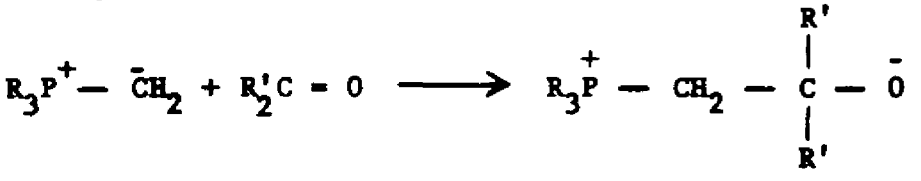


Both of these processes are encouraged by an increase in temperature and a removal of ammonia.

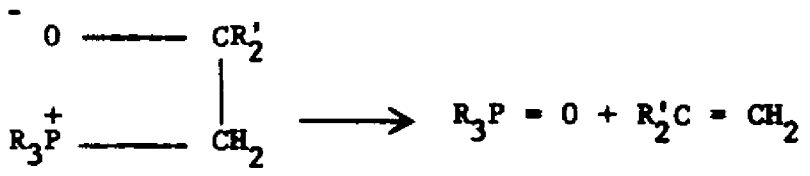
In the reaction with cyclohexanone, this ketone is added to the dimethylmethylenetin while the reaction mixture is still cold and while the ylid is well solvated by the ammonia molecules. The monomeric ylid is then free to react with the carbonyl group and form the molecular addition complex:



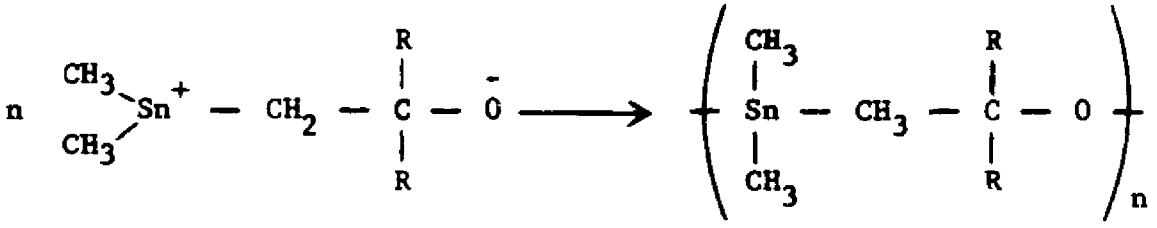
Similar types of molecular addition complexes (betaines) are believed to be formed in the Wittig reaction (17), (34), (36), (37), of phosphorus ylids.



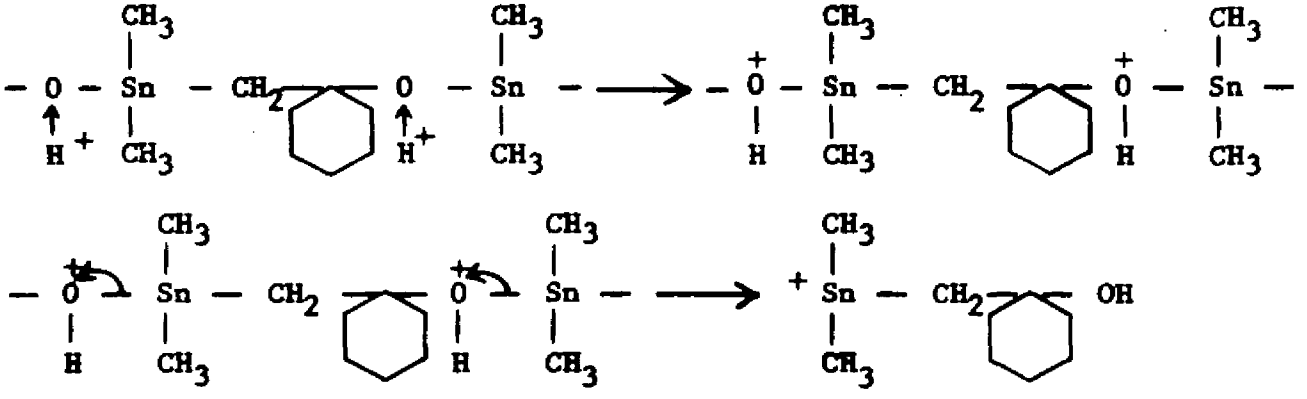
Because of the relative reluctance of phosphorus to form pentacovalent compounds, the phosphorus betaines apparently do not polymerize, but decompose on heating to form the phosphine oxide and an olefin (17), (32), (34), (35).

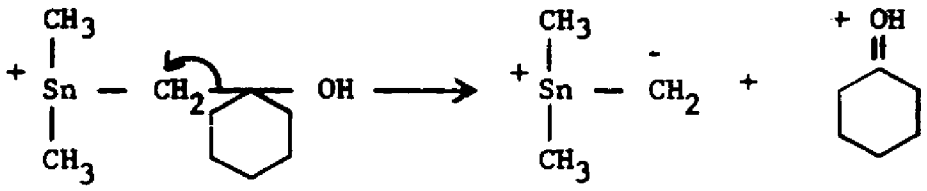


Tin, unlike phosphorus and the Group V elements, readily forms four covalent bonds. The betaine formed from the tin ylid and a carbonyl compound, therefore, should readily form a cyclic or linear polymer:

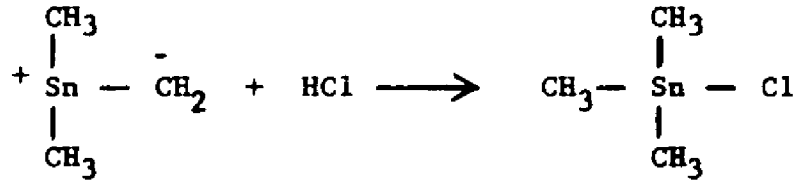


The molecular addition complex of methylenedimethyltin with cyclohexanone was treated with hydrochloric acid. An oil was formed which was found to consist of trimethyltin chloride and cyclohexanone. These materials may be accounted for by assuming an electrophilic attack by hydrogen ion on oxygen followed by several electronic shifts:

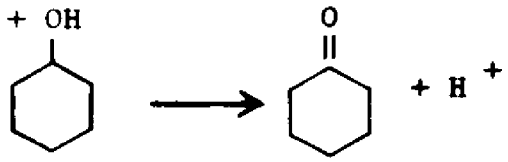




The ylid produced can then add hydrochloric acid to give trimethyltin chloride:



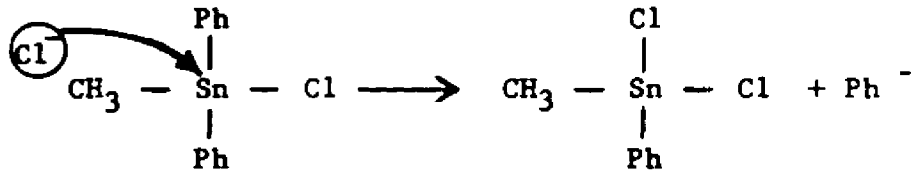
The oxonium ion can split out a proton resulting in the formation of the observed cyclohexanone:



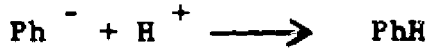
The reaction of methylenediphenyltin with formaldehyde (as trioxane) was very similar to the preceding reaction. Before the sym-trioxane was added, however, the ammonia was allowed to evaporate. This was necessary in order that all the formaldehyde not be removed by reaction with ammonia in the formation of urotropin (hexamethylenetetramine). In order that the removal of ammonia might not too adversely affect the stability of the ylid, the reaction temperature was maintained at -70° during the removal of the ammonia and during the addition of sym-trioxane. The molecular addition complex was again soluble in tetrahydrofuran, and the hydrolysis product gave an oil on treatment with hydrochloric acid. The suspected products of the reaction were methylphenyltin dichloride and methyldiphenyltin chloride. The latter compound can be accounted for by a

mechanism identical to that proposed for the methylenedimethyltin-cyclohexanone polymer.

The presence of methylphenyltin dichloride can be explained by simply considering a chloride ion nucleophilic displacement on methyldiphenyltin chloride:

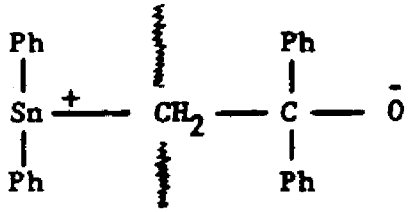


The formation of benzene is likely, but was not demonstrated:



The formaldehyde formed in the hydrolysis step was presumably lost as the gas; the hydrolysis product did not contain any formaldehyde, and an effervescence was observed but the gas was not collected.

The reaction of methylenediphenyltin with benzophenone failed to give any isolable molecular addition complexes. Apparently the internal steric strain which would be present in the betaine is sufficiently large to prevent its formation:

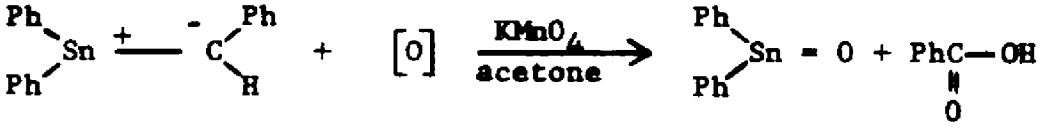


Attempted reaction of stannoethylenes with esters. - The fact that the stannoethylenes formed polymeric molecular addition complexes with cyclohexanone and formaldehyde, indicated that they also might be able to complex esters by analogy with the well-known behavior of Grignard reagents and other carbanionic structures. A sample of methylenedimethyltin was prepared in the usual manner in ammonia and tetrahydrofuran. The ammonia was removed while the temperature was maintained at 0° to discourage polymer formation and disproportionation. Methyl acetate was then added, but no reaction was observed. The fact that the carbonyl group in esters is not as strongly polarized as that in aldehydes and ketones apparently precludes the formation of an addition complex between the ylids and esters.

Attempted reaction of stannoethylenes with carbon dioxide. - Another reagent well known for its ability to react with carbanionic centers is carbon dioxide. Several attempts were made to react methylenedimethyltin with carbon dioxide in the form of Dry Ice. In none of these attempts was any product isolated other than the unreacted ylid. A possible explanation for this lack of reactivity is the relatively high energy of activation for the reaction involving $CO_2$, as compared with the corresponding reaction with aldehydes and ketones. It is noteworthy that in each case in which Dry Ice was present the yield of ylid was about 85%. This increased yield may be attributed to the fact that Dry Ice causes a 45°

lowering of the reaction temperature, which discourages polymerization and disproportionation of the ylid.

Oxidative cleavage of a stannoethylene.- If, as the formation of molecular addition complexes with carbonyl compounds indicates, the ylid structure is present in the stannoethylenes, then oxidation of the ylid in the monomeric state should give rise to the oxide of the dialkyl or diaryltin compound in question, and an aldehyde or acid. Benzylidenediphenyltin was selected as the ylid to be oxidized, since the products of oxidation (diphenyltin oxide and benzoic acid) should be readily identifiable. This ylid was prepared in the usual way in liquid ammonia. After allowing the ammonia to evaporate, and filtering the resulting tetrahydrofuran solution, an acetone solution of potassium permanganate was added. The products of this reaction were, as expected, diphenyltin oxide and benzoid acid.



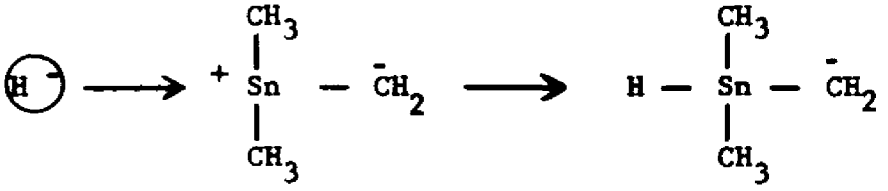

Reaction of metal hydrides with stannoethylenes. - Calamari (1) had unsuccessfully attempted catalytic hydrogenation of a number of organotin ylids using several catalysts. During the present investigation, it was felt that complex metal hydrides might be more suitable reagents for the reduction of these ylids. Catalytic hydrogenation has long been conceded to proceed via a four-center transition state, thereby giving cis addition of hydrogen (27). Reductions

with complex metal hydrides, on the other hand, proceed presumably by initial attack of hydride ion (25). Since a semipolar double bond exists in the organotin compounds in question, it seemed likely that a hydride ion would easily attack the somewhat electron-impoverished tin atom. Methylenedimethyltin was chosen for this experiment because reduction should give rise to the known trimethyltin hydride. Trimethyltin hydride (b.60°), (12), and tetrahydrofuran (b.64-66°), (13), boil sufficiently near the same temperature as to make separation extremely difficult; therefore, it was considered unwise to attempt the reaction in tetrahydrofuran, which had been used for previous experiments, and tetrahydropyran (b.81-82°), (14), was used instead.

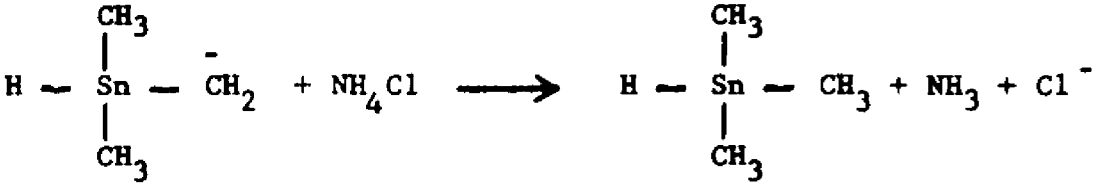
Since the monomeric ylid is most stable at low temperatures and in the presence of a large excess of ammonia, it was first decided to use a complex metal hydride which was not sensitive to ammonia. The only hydride available which was inert toward liquid ammonia was lithium borohydride. When this reagent was added to the methylenedimethyltin in liquid ammonia and tetrahydropyran, no reduction was observed. The only product isolated was the unreacted ylid.

Since lithium borohydride is not as vigorous a reducing agent as lithium aluminum hydride, it was decided that an attempt at reduction should be made using the latter reagent. One problem at once presented itself. Lithium aluminum hydride reacts vigorously with ammonia (7). This fact necessitated the preliminary

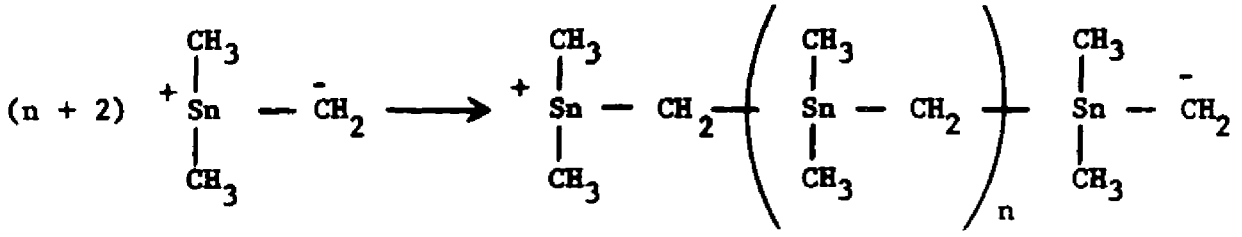
removal of ammonia at relatively low temperatures, ca. 0°. The resulting tetrahydropyran suspension was filtered, then lithium aluminum hydride added with the exclusion of moisture. The reaction anticipated is that illustrated below:



The resulting carbanion of such a reaction could be converted to trimethyltin hydride by the addition of ammonium chloride:

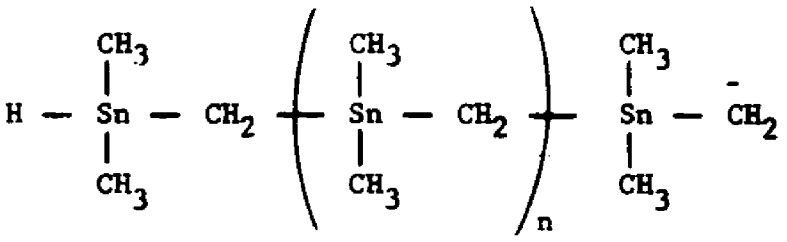


A careful search of the reaction products did not reveal the presence of any trimethyltin hydride. Instead a yellow oil was isolated which had a rather constant molecular weight of about 450. The infrared spectrum of this material indicated the presence of a hydroxyl function. These observations may be explained by assuming a preliminary dimerization and trimerization of the monomeric ylid:



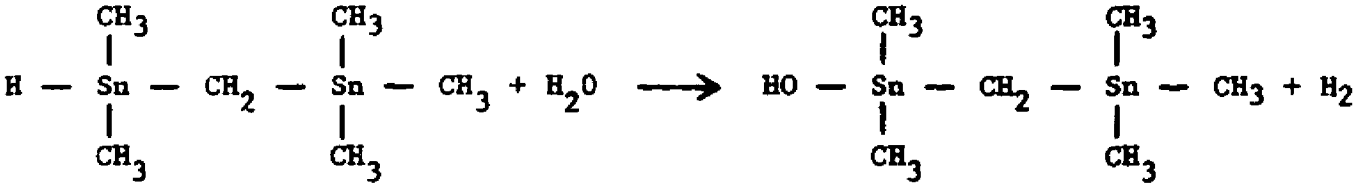
n = 0 or 1

This partial polymerization is likely, since the removal of ammonia tends to encourage such chain formation. The hydride ion then attacks the dimer or trimer resulting in formation of carbanions of the following type:



n = 0 or 1

This carbanion is then converted to the neutral polymeric tin hydride shown below by the action of ammonium chloride. Apparently this tin-hydrogen bond is quite fragile and susceptible to hydrolysis by traces of moisture, resulting in the formation of the corresponding tin hydroxide:

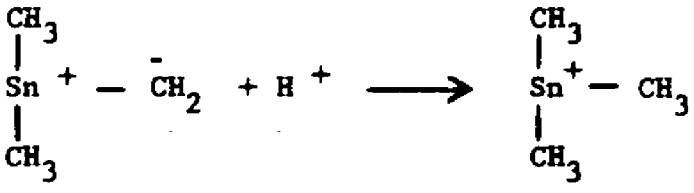


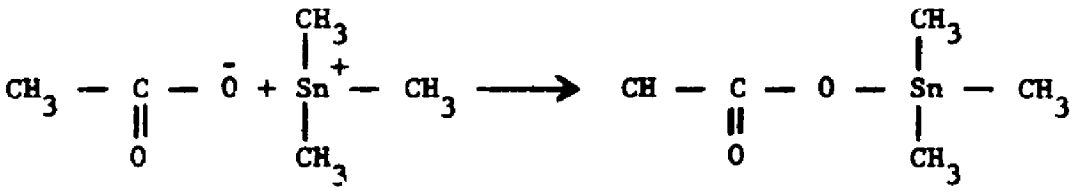
Several factors seem to indicate that this is the case. First of all, the molecular weight remained approximately constant with time, ca. 450. If the oil isolated had been the unreacted ylid, then polymerization would have been quite rapid, resulting in a much higher molecular weight polymer than was observed. The molecular weight of the hydroxide of the ylid trimer would be 504; that of the dimer would be 341. The observed value of 450 indicates that a mixture of the two is likely.

Secondly, the presence of a strong infrared absorption band indicative of hydroxyl argues strongly for the hydrolysis step.

Reaction of stannoethylenes with carboxylic acids. - Kraus and Greer (20) had observed that when methylenedimethyltin was treated with hydrochloric acid, trimethyltin chloride was formed. Although this material might result from the addition of hydrochloric acid to the monomeric ylid, it is also possible to account for it by the action of this acid on the polymerized stannoethylene. If a weaker acid were employed, it would seem unlikely that it could cleave the polymer; hence, it was decided to react acetic acid with methylenedimethyltin, since acetic acid should react quite readily with the ylid bond without disturbing other carbon-tin bonds.

The ylid was prepared in the usual manner. The ammonia was then removed while the temperature was maintained at 0°. Glacial acetic acid was added, and the reaction allowed to proceed at room temperature. A 42.2% yield of the expected trimethyltin acetate was obtained.

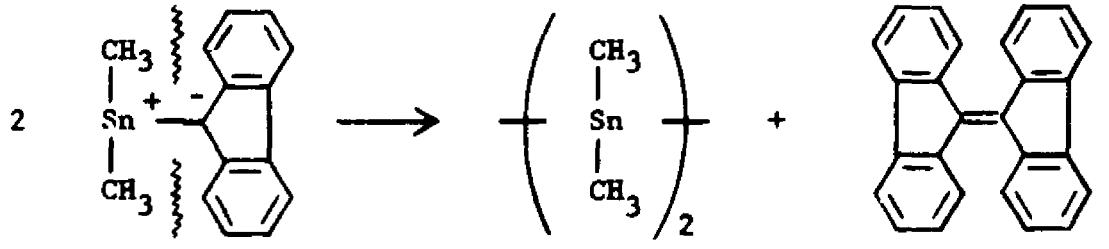




In order to demonstrate the fact that acetic acid was not capable of cleaving the polymer to the observed trimethyltin acetate directly, a sample of poly(methylenedimethyltin) was dissolved in tetrahydrofuran, and treated with acetic acid under the same reaction conditions as were employed with the monomeric ylid. No trimethyltin acetate was obtained.

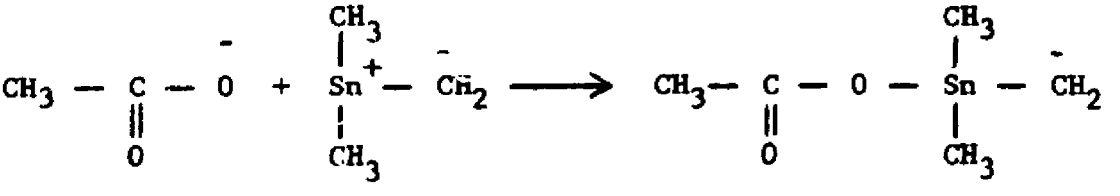
The effects of variation in acid strength and steric requirements were examined by reaction of methylenedimethyltin with benzoic acid and p-nitrobenzoic acid. The same reaction conditions as were employed with the acetate were used. A 40.2% yield of trimethyltin benzoate and a 5.6% yield of trimethyltin p-nitrobenzoate were obtained. Since benzoic acid and p-nitrobenzoic acid are somewhat stronger acids than acetic acid, it seemed probable that the yields of these benzoates should be higher than the corresponding acetate. Since this was not observed, it must be concluded that steric factors, or differences in the techniques of product isolation, or a combination of both must be causing the reduction in yield. The aromatic ions are much larger than the acetate ion. This certainly could be a contributing factor to the observed reduced yield. Also, the aromatic trialkyltin compounds were separated from the reaction mixture by vacuum sublimation. In the case of trimethyltin p-nitrobenzoate especially, this could account for the reduction in yield. Heating these materials for several hours at relatively high temperatures could cause partial decomposition and consequently reduce the yield of product.

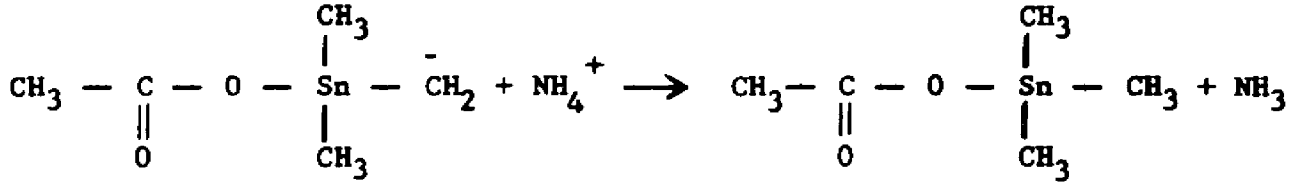
Because of the fact that acetic acid formed acetates so easily when reacted with ylids, an attempt was made to trap dimethyl-9-fluorenylidenetin as the acetate. A tetrahydrofuran solution of 9,9 dichlorofluorene was added to a solution of dimethyltin disodium in ammonia. When the ammonia had evaporated, an excess of glacial acetic acid was added. Instead of the expected dimethyl-9-fluorenylidenetin acetate, only bidiphenylene-ethylene was isolated. This product can be accounted for by assuming a disproportionation of the sterically-strained ylid:



The polymeric dimethyltin would not be soluble in tetrahydrofuran, and would be removed during the initial filtration.

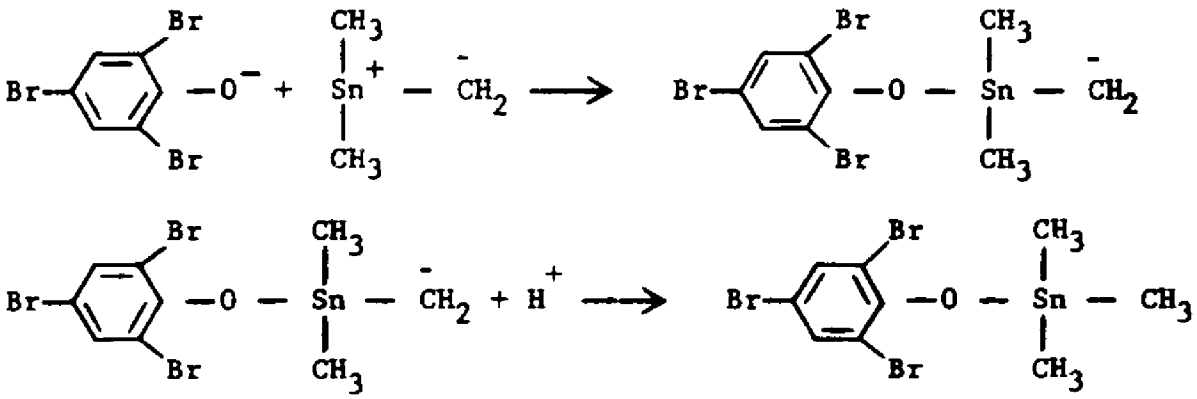
Reaction of stannoethylenes with ammonium acetate. - Since the reaction of acetic acid with methylenedimethyltin proceeded so easily, it was felt that there was a possibility that this ylid might also react with ammonium acetate. This reaction would presumably proceed through an initial attack of acetate on tin, followed by protonation.





An excess of ammonium acetate was added to methylenedimethyltin in liquid ammonia and tetrahydrofuran. This mixture was then stirred for four hours. A 36.32% yield of the expected trimethyltin acetate was obtained. The reaction of either acetic acid or ammonium acetate with methylenedimethyltin constitutes the best and most straightforward method for the preparation of trimethyltin acetate yet reported.

Attempted reaction of phenols with stannoethylenes. - Since organic acids react so readily with organotin ylids, it was felt that perhaps activated phenols, even though their acidity is relatively weak, might also add to the stannoethylenes. The reaction of 2,4,6-tribromophenol with methylenedimethyltin was attempted. If the addition had proceeded as was anticipated, then trimethyltin-2,4,6-tribromophenoxide should result:



The only compounds present in the reaction mixture were the unreacted phenol and ylid. It is apparent, then, that even activated phenoxide ions are not sufficiently nucleophilic to attack the electron-depleted centers of organotin ylids, and form stable tin-oxygen bonds.

Structure of organotin ylids. - Calamari (1) had observed that it was not possible to isolate the highly conjugated, but also highly strained, ylid, 9-fluorenylidenediphenyltin. Instead of this material, he isolated its disproportionation products - bidiphenyleneethylene and diphenyltin. During the course of the present investigation an attempt was made to prepare diphenylmethylenediphenyltin. The only products isolated were the disproportionation products of this ylid - tetraphenylethylene and diphenyltin. These results indicate that when steric strain exists in the ylid, then disproportionation will be favored over polymerization as the mode of ylid decomposition. Both processes presumably are always operating, but disproportionation is a far more serious problem when conditions of steric strain exist. Polymerization of the ylid can be minimized by operating at very low temperatures, and in the presence of a large excess of ammonia, but disproportionation is not seriously discouraged by these factors.

One may interpret all of the known chemical properties of the stannoethylenes in terms of an ylid structure. The slow rate of polymerization of methylenedimethyltin and its aromatic analogues is clearly explained by such a structure. One would expect

a pure polarized bond to react almost instantly in any situation; a double-bonded structure should be relatively stable. Hence, since an organotin ylid would be a hybrid of the two (16), it should be expected to polymerize at a moderate rate. The most significant difference between organotin ylids and ylids of Groups V and IV is that in the case of organotin ylids the double-bonded resonance structure makes a relatively greater contribution to the true structure than does the polarized resonance form. In ylids of Groups V and VI, the polarized form is relatively more important. This tendency to form four covalent bonds is manifest in the facile chain formation inherent in many of the organotin ylids studied. Polymer formation is not a problem in the case of Groups V and VI ylids since these elements are quite reluctant to form five or six covalent bonds. Typical Groups V and VI ylids decompose by disproportionation rather than by polymerization (3), (30).

In light of the above evidence it seems evident that the ylid structure is present in the stannoethylenes.

# EXPERIMENTAL PART

## Introduction

The first section of this chapter contains the experimental details of the reactions involved in this paper. The second section deals with the method employed for the quantitative estimation of tin in organotin compounds. It also outlines the procedures used for molecular weight determinations.

## Preparation of Dimethyltin Disodium

The procedure followed in this preparation and that followed for methylene dimethyltin is essentially that of Kraus and Greer (17). A one liter three-neck round bottom flask was fitted with a Dry Ice reflux condenser, an automatic stirrer, and an ammonia inlet connection. Into the flask was introduced 21.97 g. (0.1 mole.) of dimethyltin dichloride. Three hundred milliliters of anhydrous ammonia were gradually introduced into the vessel over a period of about one hour. When stirred, the dimethyltin dichloride formed a chalky suspension in the ammonia. To this mixture was added 9.2 g. (0.4 g. atom) of sodium (as pea-sized lumps) over a period of thirty minutes with constant stirring. Several color changes took place during the addition of the sodium. As the first 0.2 g. atom was added, the suspension changed from white to cream, then from cream to yellow and

became quite viscous. As the second 0.2 g. atom was gradually added, the reaction mixture thinned considerably, and the yellow color was replaced by a pale orange hue. By the time the last portion of sodium was introduced, the ammonia solution had taken on an intensely red color which appeared black by reflected light. The mixture was stirred for one hour after the addition of the last portion of sodium, and the resulting dimethyltin disodium was used immediately without isolation.

## Preparation of Diphenyltin Disodium

The general procedure used for the preparation of dimethyltin disodium was employed. One-tenth of a mole (34.38 g.) of diphenyltin dichloride was placed in a one liter three-neck flask fitted as before, and 300 ml. of ammonia was run in over a period of one hour. As with its dimethyl analogue, the diphenyltin dichloride formed a chalky white suspension in the ammonia. Sodium (9.2 g., 0.4 g. atom) was slowly added to this suspension. The reaction mixture changed from white to tan, then from tan to dark brown during the addition of the first 0.2 g. atom of sodium. The reaction mixture again became quite thick during this period. As the second 0.2 g. atom of sodium was added, the brown slurry thinned considerably, and the color was completely changed to red. When the last amount of sodium had been added, the final color was intensely red (black by reflected light). The mixture was then stirred for one hour. The diphenyltin disodium was not isolated.

## Preparation of Methylenedimethyltin

To an ammonia solution of 0.1 mole dimethyltin disodium prepared *in situ* was added 8.5 g. (0.1 mole) of methylene chloride in 100 ml. of anhydrous tetrahydrofuran with mechanical stirring. During the addition of halide, the intense red color of the reaction mixture was discharged. Stirring was continued for one hour to insure completeness of reaction. Next, the ammonia was allowed to evaporate. The resulting ether suspension was filtered. A large amount of solid polymeric material was removed in this manner. The filtrate was stripped of solvent under reduced pressure; a tan viscous liquid remained. This liquid was distilled in a Hickman still. A pale yellow oil distilled from 150° to 200° at 0.05 mm. Hg with some decomposition in the still. The yield was 4.2 g. (25.8%).

*Analysis*. Calculated for $C_3H_8Sn$: C, 22.13; H, 4.95; Sn, 72.92; M.W., 162.79. Found: C, 21.33; H, 4.93; Sn, 72.51; M.W., 677.

## Preparation of Benzylidenediphenyltin

One-tenth of a mole (16.1 g.) of freshly distilled benzylidene chloride in 100 ml. of anhydrous tetrahydrofuran was slowly added to a suspension of 0.1 mole of diphenyltin disodium prepared *in situ* in 300 ml. anhydrous ammonia. The intensely red color of the original solution was discharged. The ammonia was allowed to evaporate, and the resulting tetrahydrofuran suspension filtered. Again, there was much polymeric material removed by this operation.

The tetrahydrofuran was stripped from the filtrate leaving 9.4 g. (25.9%) of a thick brown oil which could not be distilled.

Analysis. Calculated for $C_{19}H_{16}Sn$: C, 62.86; H, 4.44; Sn, 32.70; M.W., 363.02. Found: C, 62.98; H, 4.41; Sn, 31.94; M.W., 790.

## Reaction of Methylenedimethyltin with Cyclohexanone

One-tenth of a mole (16.27 g.) of methylenedimethyltin was prepared as previously described. This was not isolated from the ammonia tetrahydrofuran mixture; instead, 19.6 g. (0.2 mole) of cyclohexanone in 100 ml. of anhydrous tetrahydrofuran was added and the mixture stirred for one hour. The ammonia was then allowed to evaporate. The reaction mixture was refluxed for one hour, then filtered. Very little polymeric material remained as indicated by the fact that the filter cake was almost entirely soluble in water. The filtrate was warmed with 5% hydrochloric acid for one hour, during which time the tetrahydrofuran was allowed to boil off. The resulting aqueous mixture was extracted several times with benzene and the extracts combined.

A small portion of this benzene solution was analyzed by gas chromatography. The chromatogram showed no trace of methylene cyclohexane, which might have been anticipated by comparison of this reaction with Wittig's olefin synthesis (35).

To another small portion of benzene solution was added several drops of 2,4 dinitrophenylhydrazine test solution. After warming

several minutes an orange precipitate began to form. The precipitate was filtered and then recrystallized from ethanol. The resulting yellow needles melted from 159°-160.5°: reported melting point for the 2,4-dinitrophenylhydrazone of cyclohexanone (28), 162°.

The remainder of the benzene solution was fractionally distilled. After the benzene was essentially removed, the pressure was slowly reduced to 10 mm. Hg. A colorless liquid distilled from 99°-103°. This fraction weighed 17.2 g. and proved to be cyclohexanone. Increasing the pot temperature to 200° did not cause distillation of any of the residual brown oil. This residue was found to contain chlorine and had an infrared spectrum very similar to that of trimethyltin chloride. This oil could not be induced to crystallize. It weighed 18.1 g. (This corresponds to a 90.6% yield of trimethyltin chloride).

Reaction of Methylenediphenyltin with sym.-Trioxane

Diphenyltin disodium was prepared by the addition of 9.2 g. (0.4 g. atom) of sodium to 34.38 g. (0.1 mole) of diphenyltin dichloride in 300 ml. of anhydrous ammonia. To the resulting red solution was added 300 ml. of freshly distilled tetrahydrofuran. The ammonia was induced to evaporate giving a dark green solution. A slight excess of methylene chloride (9.4 g., 0.11 mole) in 50 ml. of anhydrous tetrahydroguran was slowly added while the reaction temperature was maintained at -70°C. The color of the reaction mixture after halide addition was deep greenish brown. A large excess

(15 g., 0.5 mole) of sym.-trioxane was added and the mixture refluxed for three hours.

The tetrahydrofuran suspension was then filtered. The residue was composed of sodium chloride, for the most part, together with a small amount of water-insoluble polymeric material.

The filtrate was heated under reduced pressure to remove all solvent; then the resulting oil was warmed with 5% hydrochloric acid to remove all remaining trioxane and to hydrolyze the adduct. The acid mixture was extracted several times with benzene and the extractions combined. A small aliquot was removed and several drops of 2,4 dinitrophenylhydrazine test solution added. The mixture was warmed for several minutes, but no precipitate formed.

After removing the benzene from the remaining solution, an attempt was made to distill the residue. At a pressure of 1 mm. of Hg and a pot temperature of 200°, none of the brown oil distilled. The infrared spectrum of this oil was not inconsistent with that of a mixture of phenylmethyltin dichloride and methyldiphenyltin chloride, but neither of these compounds could be positively identified in the brown oil. The oil weighed 28.3 g. and was found to contain chlorine.

## Attempted Reaction of Methylenediphenyltin with Benzophenone

Methylenediphenyltin (0.1 mole) was prepared using the procedure given above. The ammonia was allowed to evaporate. To the

resulting tan suspension was added 18.2 g. (0.1 mole) of benzophenone in 100 ml. of anhydrous tetrahydrofuran. This slurry was stirred for two hours at 25°, then filtered, giving 300 ml. of solution. The filter cake was extracted with water to remove sodium chloride. A large amount of tan water insoluble residue remained.

A 50 ml. portion of the filtrate was stripped of solvent and 4.0 g. of a brown oil was obtained. This oil contained tin, but no halogen. One gram of this material was dissolved in a mixture of 5 ml. of chloroform and 20 ml. of cyclohexane. This solution was placed on a column of chromatographic grade alumina, and developed using a 1% solution of chloroform in cyclohexane. Fractions were collected in 5 ml. portions until a total of 100 ml. was obtained. These were labeled #1 to #20. The solvent was allowed to evaporate from these fractions. Fractions #7, #8, and #9 contained a white solid material which proved to be benzophenone. It weighed .39 g. Fractions #14, #15, and #16 contained a thick brown oil. The infrared spectrum of this material was identical to that for polymeric methylenediphenyltin.

## Attempted Reaction of Methylenedimethyltin with Methyl Acetate

One-tenth of a mole (16.2%) of methylenedimethyltin was prepared using the standard procedure. The ammonia was allowed to evaporate, then 0.1 mole (7.4 g.) of anhydrous methyl acetate was added. The reaction mixture was stirred for two hours at 0°, then allowed to reach room temperature while stirring was continued for

another hour. The resulting suspension was filtered, and the filtrate fractionated. Almost all of the methyl acetate, i.e., 6.4 g., was recovered by this process. After removing the remaining tetrahydrofuran, 6.1 g. (37.5%) of methylenedimethyltin was obtained. Identification was based on the infrared spectrum.

## Attempted Reaction of Methylenedimethyltin with Carbon Dioxide

One-tenth of a mole (16.27 g.) of methylenedimethyltin was prepared using the standard procedure. An excess (8.8 g.) of carbon dioxide in the form of Dry Ice was then added to the solution while it was vigorously stirred. This reaction mixture was stirred for one hour at $-33^{\circ}$, then the ammonia allowed to evaporate over the next three hours. Filtration of the reaction mixture gave a pale yellow tetrahydrofuran filtrate. Upon evaporation of the tetrahydrofuran, 14.1 g. (86.1%) of methylenedimethyltin was obtained. Identification was again based on the infrared spectrum of the material.

## Oxidation of Benzylidenediphenyltin

One-tenth of a mole (36.3 g.) of benzylidenediphenyltin was prepared by the method given above. It was not isolated, but was used in tetrahydrofuran solution. To this solution was added 16.0 g. (0.11 mole) of potassium permanganate in 500 ml. of dry acetone. This mixture was warmed for four hours; then the acetone and tetrahydrofuran were boiled off. The black residue which remained was extracted several times with ethanol. Upon removal of most of the alcohol and

the addition of cold water, a white precipitate resulted. This material melted from 120°-121°. It was proved to be benzoic acid by its infrared absorption spectrum. The yield was 2.1 g. (17.4%, based on benzylidene chloride).

## Attempted Reduction of Methylenedimethyltin Using Lithium Borohydride

One-tenth of a mole (16.27 g.) of methylenedimethyltin was prepared as previously described except for the fact that the tetrahydrofuran was replaced with tetrahydropyran. To the ammonia tetrahydropyran solution of this compound was added 2.2 g. (0.1 mole) of lithium borohydride. This mixture was stirred overnight at room temperature, then filtered. The filtrate was very carefully fractionated, but none of the anticipated trimethyltin hydride could be detected in the distillate.

## Attempted Reduction of Methylenedimethyltin Using Lithium Aluminum Hydride

One-tenth of a mole (16.27 g.) of methylenedimethyltin was prepared using tetrahydropyran as described in the experimental procedure above. The reaction mixture was maintained at 0° for one hour while it was vigorously stirred to remove most of the ammonia. The reaction vessel was then evacuated to 20 mm. of Hg for thirty minutes to remove the last traces of ammonia. The resulting slurry was filtered to remove sodium chloride and various polymeric tin compounds. To the filtrate was slowly added 3.8 g. (0.1 mole) of

lithium aluminum hydride. The reaction mixture was stirred for one hour at room temperature, then warmed to 88° and stirred an additional hour.

Careful fractionation of the filtered solution again showed no trace of the anticipated trimethyltin hydride. Instead, a yellow oil was isolated which could not be distilled. A molecular weight determination was made twelve hours after the oil was isolated. This gave a value of 446. Another molecular weight determination was made twenty-four hours later. The value was then 460. The infrared spectrum was almost identical to that of freshly distilled methylenedimethyltin. The only major difference was a strong absorption peak at 2900 mu. This indicated the presence of a hydroxyl function.

Reaction of Methylenedimethyltin with Acetic Acid

One-tenth of a mole (16.27 g.) of methylenedimethyltin was prepared using the original procedure given above. The ammonia was allowed to evaporate. Six grams (0.1 mole) of glacial acetic acid in 100 ml. of anhydrous tetrahydrofuran was slowly added to the stirred reaction mixture. The resulting suspension was stirred for two hours at 25°, then filtered. Controlled evaporation of the tetrahydrofuran filtrate afforded 9.4 g. (42.2% based on methylene chloride) of trimethyltin acetate, m.p. 195°-196°: reported (21), 196°-197°.

Analysis. Calculated for $C_5H_{12}O_2Sn$: Sn, 51.74. Found: Sn, 50.96.

## Reaction of Polymeric Methylenedimethyltin with Acetic Acid

Methylenedimethyltin (0.1 mole) was prepared using the standard procedure. The ammonia was allowed to evaporate and the resulting tetrahydrofuran solution filtered. The filtrate was stripped of solvent and a thick yellow oil remained. This was placed in a vacuum desiccator for one week. At the end of this period the yellow oil had become extremely viscous. It weighed 16.3 g. (56.8% based on methylene chloride). An attempt was made to determine the molecular weight of the material cryoscopically (See p. 46), but no depression of the freezing point of benzene was observed.

To 2.9 g. (0.01 mole of monomeric methylenedimethyltin) of this polymer in 100 cc. of tetrahydrofuran was added 1.2 g. (0.02 moles) of acetic acid. This solution was stirred for two hours at 25°. Upon evaporation of the tetrahydrofuran a brown oil was obtained. This oil was dissolved in methylene chloride and extracted with water. The organic layer was carefully freed of solvent using an aspirator. No trace of trimethyltin acetate could be found in the resulting brown oil.

## Reaction of Methylenedimethyltin with Benzoic Acid

Methylenedimethyltin was prepared using the standard procedure for one-tenth of a mole of material. The ammonia was allowed to evaporate; then 12.21 g. (0.1 mole) of benzoic acid in 100 ml. of tetrahydrofuran was slowly added. The mixture was

stirred for two hours at 25°, then filtered. Upon evaporation of solvent from the tetrahydrofuran solution, a thick brown oil was obtained which weighed 17.0 g. This oil was placed in a vacuum sublimator and heated at 150° and .05 mm. of Hg for four hours. Two zones of white crystals were formed on the condensing walls of the sublimator. The leading zone afforded 4.9 g. (40.2%) of benzoic acid. The trailing zone weighed 5.9 g., but did not melt sharply. Recrystallization of this material from carbon tetrachloride gave 4.7 g. of a white solid which melted from 211°-212.5°. This material was identified as trimethyltin benzoate.

Analysis. Calculated for $C_{10}H_{14}O_2Sn$: Sn, 41.68. Found: Sn, 41.03%.

## Preparation of 9,9-Dichlorofluorene

The procedure of Smedley (29) was used, for the most part, in this preparation. One-tenth of a mole (18 g.) of fluorenone was heated with 22.0 g. (0.11 mole) of phosphorus pentachloride in an oil bath at 160° for one hour. The reaction mixture was cooled and water added to decompose the excess phosphorus pentachloride. The crude yellow product was recrystallized from ether and then from petroleum ether. Colorless needles were obtained which melted at 99-100°: reported (29), 99-100°.

## Attempted Preparation of Dimethyl-9-Fluorenylidentin Acetate

To an ammonia solution of 0.1 mole of dimethyltin disodium prepared *in situ* was added 23.5 g. (0.1 mole) of 9,9-dichlorofluorene in 100 ml. of anhydrous tetrahydrofuran. During the addition of the dihalide the intense red color of the reaction mixture was discharged. The mixture was stirred for one hour to insure completeness of reaction. The ammonia was allowed to evaporate. An excess, 12.0 g. (0.2 mole), of glacial acetic acid in 100 ml. of tetrahydrofuran was slowly added and the mixture stirred constantly. Stirring was continued for two hours at 25° after the addition of acid. The reaction mixture was then filtered and the filtrate stripped of solvent. A red oil remained. This material was dissolved in methylene chloride and extracted several times with water. Fractional recrystallization of the red material remaining after drying and stripping off methylene chloride yielded 10.8 g. (69.4%) of bidiphenyleneethylene, m.p. 187-188°; reported (9), 188°. Identification was based on the melting point and the infrared spectrum.

After removal of as much of the bidiphenyleneethylene as was possible using fractional recrystallization, the remaining oil was dissolved in 10 ml. of a solution of 20% chloroform in cyclohexane. This solution was placed on an alumina column and developed using a 1% solution of chloroform in cyclohexane. Fractions of five ml. were collected until a total volume of 100 ml. was obtained. A thin orange zone was noticed from the outset and this was eluted rapidly. It was collected in the fractions #5 and #6, and was

identified as bidiphenyleneethylene.

## Reaction of Methylenedimethyltin with p-Nitro-Benzoic Acid

Methylenedimethyltin (0.1 mole) was prepared using the standard procedure. After allowing the ammonia to evaporate, 16.7 g. (0.1 mole) of p-nitrobenzoic acid in 100 ml. of anhydrous tetrahydrofuran was slowly added with mechanical stirring. The mixture was stirred at 25° for one hour after the addition of acid was complete, then filtered. After stripping off the solvent, 32.4 g. of a brown oil remained. This was placed in a vacuum sublimator and heated at 180° for six hours at 0.05 mm of Mg. A zone of pale yellow crystals weighing 2.4 g. was formed on the condensing surface of the sublimator. Upon recrystallizing, this material from chloroform, 1.9 g. (5.76% based on p-nitrobenzoic acid) of pale yellow crystals identified as trimethyltin p-nitrobenzoate was obtained. The melting point was 235° in a sealed tube.

Analysis. Calculated for $C_{10}H_{13}NO_4Sn$: Sn, 35.99. Found: Sn, 36.87.

## Reaction of Methylenedimethyltin with Ammonium Acetate

One-tenth of a mole (16.27 g.) of methylenedimethyltin was prepared using the standard procedure. To the resulting ammonia-tetrahydrofuran slurry was added 11.6 g. (0.15 mole) of ammonium acetate. This mixture was vigorously stirred for four hours at 25°;

then the ammonia was allowed to evaporate. The resulting grey tetrahydrofuran slurry was filtered and a brown solution obtained. Upon evaporation of the solvent, 14.9 g. of a brown oil remained. This was placed in a vacuum sublimator and heated at 150° for four hours at 0.05 mm. of Hg. A zone of white crystals soon formed on the condensing walls. These weighed 8.6 g. Upon recrystallization of this crude material from carbon tetrachloride, 8.1 g. (36.32% based on methylene chloride) of trimethyltin acetate melting from 196-197° was obtained.

## Attempted Reaction of 2,4,6-Tribromophenol with Methylenedimethyltin

Methylenedimethyltin (0.1 mole) was prepared using the standard procedure. When the ammonia had evaporated, 33.1 g. (0.1 mole) of 2,4,6-tribromophenol in 100 ml. of anhydrous tetrahydrofuran was slowly dripped into the vigorously stirred suspension. After the addition was complete, the mixture was stirred an additional two hours at 25° and then filtered. The tetrahydrofuran was stripped off, and 48.6 g. of a brown oil remained. This was placed in the vacuum sublimator and heated at 150° for four hours at .06 mm. of Hg. A zone of white crystals was formed which weighed 29.1 g. The material was recrystallized from benzene, and proved to be 2,4,6-tribromophenol. Identification was based on a mixed melting point with a known sample and its infrared spectrum.

The brown oil remaining in the sublimator contained no halogen. Its infrared spectrum indicated that it was polymeric methylenedimethyltin.

None of the expected trimethyltin 2,4,6-tribromophenoxide was detected.

## Reaction of Diphenyltindisodium with Diphenyldichloromethane

Diphenyltindisodium was prepared using the procedure above for one-tenth of a mole. To the dark red solution was added 23.7 g. (0.1 mole) of diphenyldichloromethane in 200 ml. of dry tetrahydrofuran. This suspension was stirred for one hour, then filtered. When evaporation of the first 100 ml. of solvent was effected, a number of colorless crystals began to precipitate from solution. The volume of this solution was further reduced to 30 ml.; it was then placed in a refrigerator at 0° overnight. The resulting crystals were filtered and dried. They weighed 14.2 g., and contained neither tin nor halogen. This material melted from 219°-221°: reported (11) for tetraphenylethylene, 221°.

## The Macro Determination of Tin

Two of the better methods available today for the quantitative estimation of tin are those of Kocheshkov (19) and of Gilman and King (10). Both are gravimetric procedures based on the total oxidation of the tin to stannic oxide. Of the two, the latter method is more generally applicable since it can be used for both volatile and non-volatile organotin compounds. The method of Kocheshkov is the more easily performed of the two, but cannot be employed in the analysis of substances such as the lower tin

tetraalkyls because of losses resulting from rather high vapor pressures of many organotin compounds. Since the compounds involved were extremely high boiling liquids so that no volatilization was anticipated, Kocheshkov's method was used in this work. The procedure outlined below is the Luijten-Van der Kerk modification (22) of Kocheshkov's method.

A small amount of the substance under investigation was placed in a quartz test tube which had previously been heated to constant weight. The compound was oxidized by means of a cold mixture of equal parts by volume of fuming nitric and fuming sulfuric acids. The tube was heated to complete the oxidation to stannic oxide and to volatilize the acid. The tube and contents were heated strongly until the weight became constant, and percent tin was calculated from the weight of the oxide.

## Molecular Weight Determinations

All molecular weight determinations were done cryoscopically in anhydrous benzene using a Beckman freezing-point apparatus according to the method of Daniels, Mathews, and Williams (5).

## SUMMARY AND CONCLUSIONS

Calamari's work (1) on the reaction of the stannoethylenes with aldehydes and ketones has been repeated. His proposal that molecular addition complexes were formed between the stannoethylenes and these carbonyl compounds has been confirmed. These polymeric addition complexes are converted to the free carbonyl compound and the tri- or dialkyltin chloride by reaction with hydrochloric acid. When the formation of the addition complex would result in a significant steric strain, the complex fails to form. Thus, benzophenone failed to undergo complex formation with methylenediphenyltin.

An attempt was made to form an addition complex between methylenedimethyltin and methyl acetate. This reaction failed, indicating that the carbonyl group in esters is not sufficiently polarized to react with organotin ylids. Presumably for the same reason, the reaction of methylenedimethyltin with carbon dioxide also failed.

Oxidation of benzylidenediphenyltin with potassium permanganate gave the expected products - diphenyltin oxide and benzoic acid.

Reduction of the stannoethylenes with complex metal hydrides was not as straightforward as oxidation. Since organotin ylids begin to polymerize in the absence of ammonia, a complex metal

hydride which was not ammonia sensitive was first chosen for the reduction. Lithium borohydride was used for the initial attempt at reduction, but no reaction was observed. Since lithium borohydride is a relatively weak reducing agent, it was decided to remove the ammonia, then use the more vigorous lithium aluminum hydride. Although removal of the ammonia permitted preliminary dimerization and trimerization of the ylid, nonetheless a moisture-sensitive tin hydride was apparently formed. This material was isolated as the corresponding tin hydroxide.

Organotin ylids react readily with organic acids or the ammonium salts of organic acids to produce tin esters. The reaction with ammonium salts of organic acids is perhaps the most convincing evidence for the existence of a semi-polar double bond in the stannoethylenes. By this reaction, two trialkyltin esters have been prepared which have previously been unreported in the literature. These are trimethyltin benzoate and trimethyltin p-nitrobenzoate.

Since the reaction of these ylids with organic acids proceeded so readily, an attempt was made to react methylenedimethyltin with the activated phenol - 2,4,6-tribromophenol. No reaction was observed.

On the basis of the chemical evidence presented above, considered in conjunction with the earlier observations of Kraus and Greer (20), and Calamari (1), there seems little doubt that the stannoethylenes have the ylid structure.

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# VITA

Timothy A. Calamari, Jr. is the son of Mr. and Mrs. Calamari of New Orleans, Louisiana. He was born there on November 12, 1936. His primary education was obtained in the public schools of New Orleans, and he received his secondary education at Jesuit High School of that city. In September, 1954, he entered Loyola University of the South. Before graduating, he received the "American Institute of Chemists' Award" for scholastic proficiency. He received his Bachelor of Science degree in Chemistry in May, 1958. In September, 1958, he entered the Graduate School of Louisiana State University. He received his Master of Science degree in January, 1961 from this university. He was a National Science Foundation Cooperative Fellow from September, 1961 to June, 1962, and a Cities Service Fellow from September, 1962 to June, 1963. A member of Phi Lambda Upsilon, he is now a candidate for the degree of Doctor of Philosophy in Chemistry.

**EXAMINATION AND THESIS REPORT**

**Candidate:** Timothy A. Calamari, Jr.

**Major Field:** Chemistry

**Title of Thesis:** Organotin Ylids

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Date of Examination:

July 26, 1963